Supporting Information

Coordination Polymers Containing Dimeric Cu_2X_2 and Polymeric $(CuI)_n$ Clusters Linked by Unsymmetrical Isomeric Pyridine-benzimidazole Linkers: Modulating Photophysical Properties by Mechanical Stimuli

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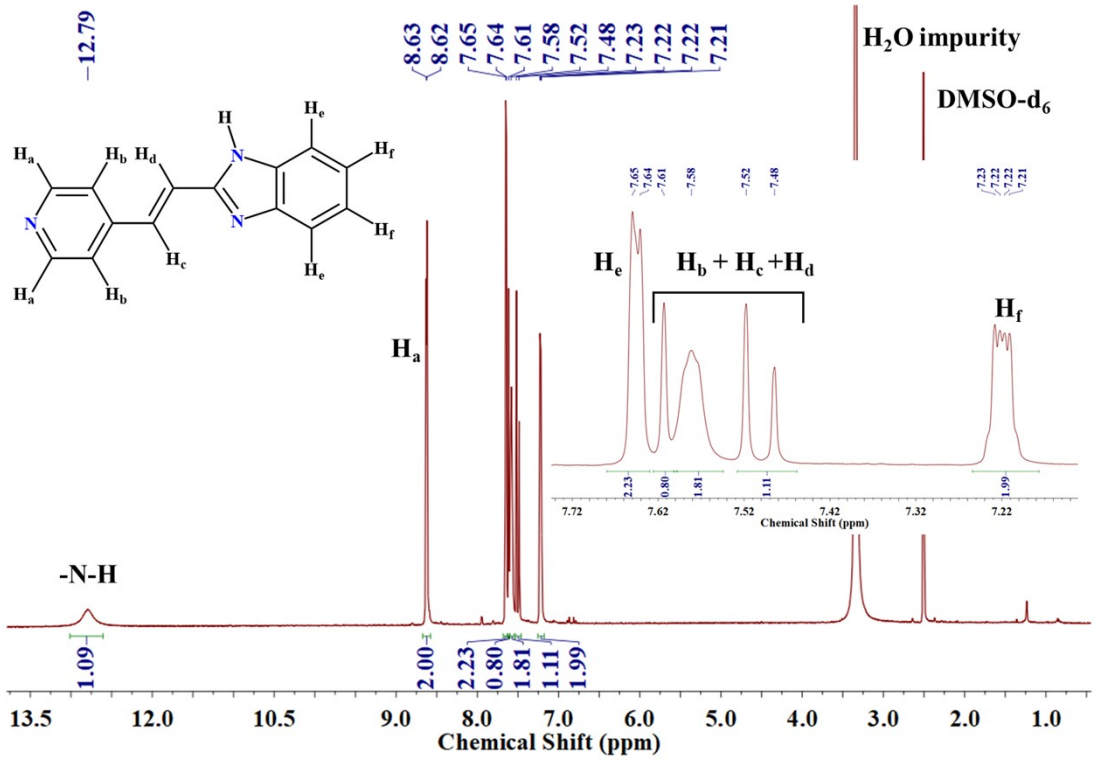
Section S1: ^{1}H NMR Spectra of ligands

(a)



(b)

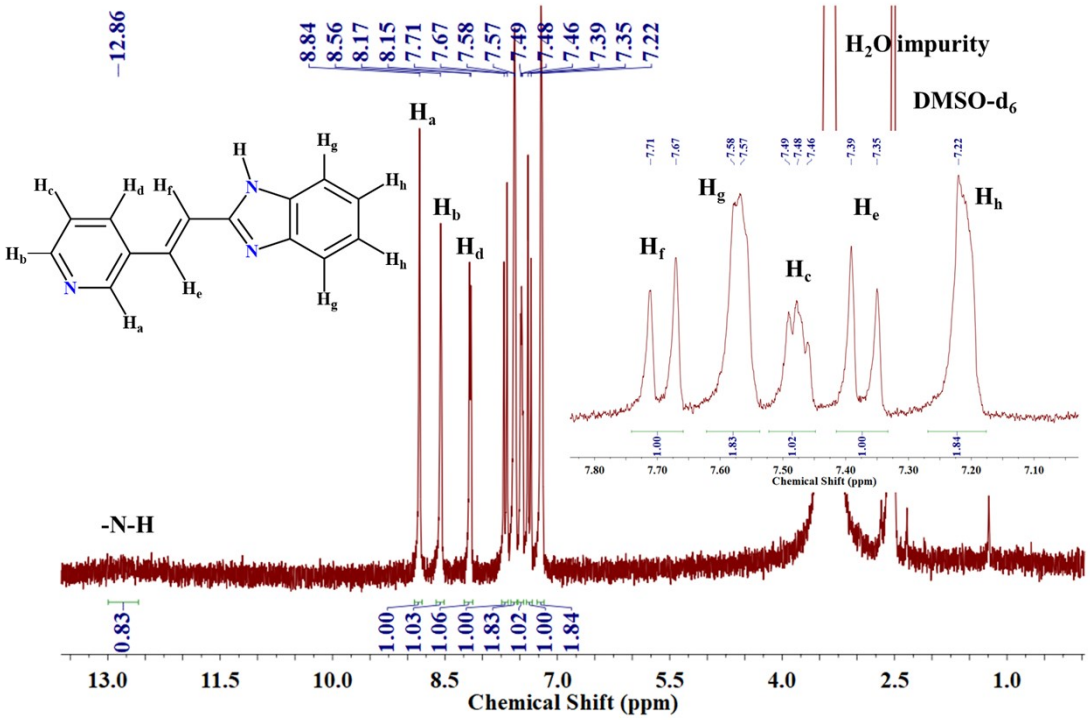


Figure S1. ^{1}H NMR (400 MHz) Spectra of (a) 4-PBI and (b) 3-PBI in DMSO-d_6.

Section S2: Crystal structure of CP1 and CP2

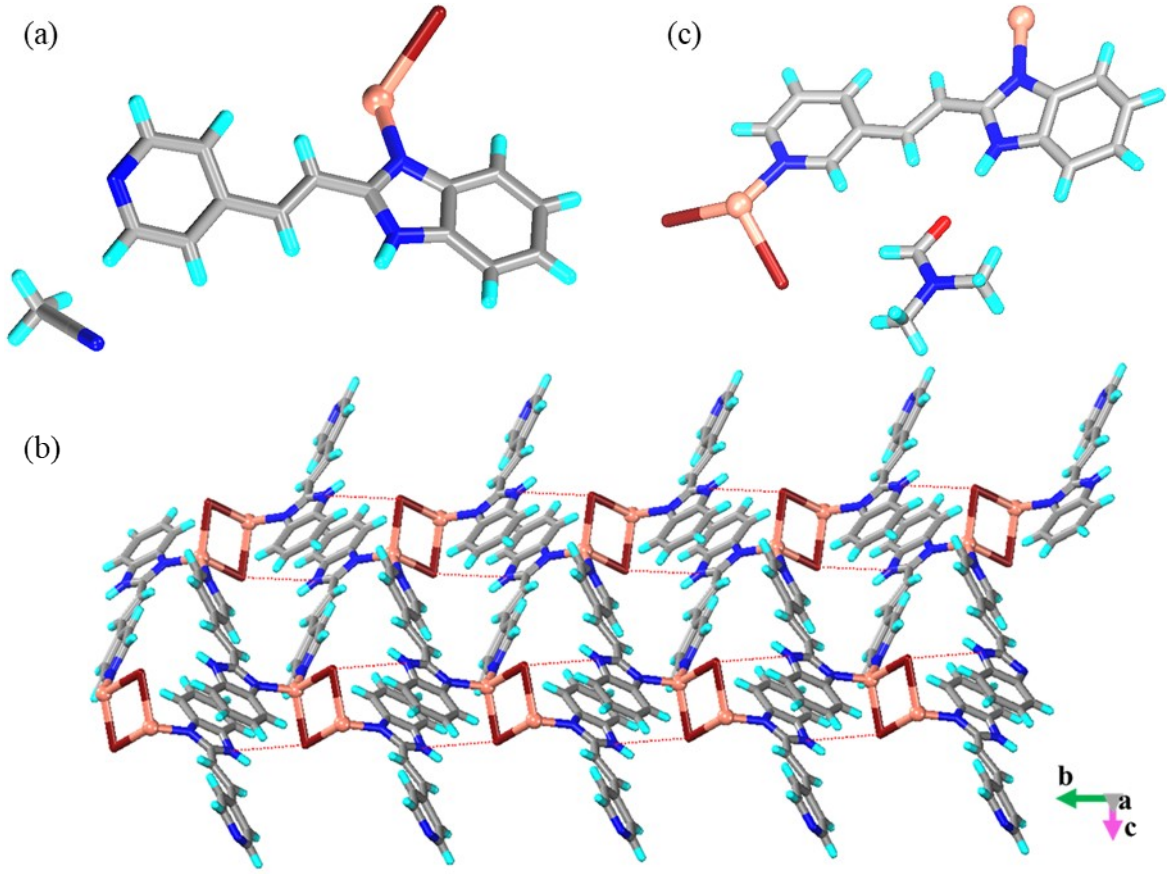


Figure S2. (a) Asymmetric unit of **CP1** and **CP2**, (b) N-H···X hydrogen bond along *b*-axis in a single 2D layer of **CP1** and **CP2** and (c) Asymmetric unit of **CP3**.

Section S3: Pertinent Crystallographic Parameters

Table S1. Crystallographic parameters for CPs

	CP1	**CP2**	**CP3**
CCDC	**2341925**	**2341926**	**2341927**
Temperature (K)	120	298	120
Crystal System	Monoclinic	Monoclinic	Orthorhombic
Space group	*C*2/c	*C*2/c	*P*na2_1
a (Å)	24.6786(19)	24.814(3)	23.585(3)
b (Å)	8.8976(7)	8.7919(9)	4.2265(5)
c (Å)	17.7969(14)	18.115(2)	20.016(2)
α (°)	90	90	90
β (°)	122.440(3)	123.312(3)	90
γ (°)	90	90	90
V (Å^3)	3298.0(5)	3302.7(6)	1995.2(4)
R-Factor (%)	1.97	2.67	6.77

Table S2. Bond distances for the CPs

CP	**Bond**	**Distance (Å)**
CP1	I1-Cu1	2.6496(2)
		2.7070(2)
	Cu1-N11	2.0223(2)
	Cu1-N21	2.0535(2)
CP2	Br1-Cu1	2.5250(5)
		2.6084(6)
	Cu1-N2	2.0031(18)
	Cu1-N1	2.035(2)
CP3	I1-Cu2	2.625(3)
	I1-Cu1	2.774(3)
		2.688(3)
	I2-Cu2	2.622(3)
		2.627(3)
	I2-Cu1	2.713(3)
	Cu1-N11	2.032(17)

	Cu2-N21	2.048(9)

Table S3. Bond angles for the CPs

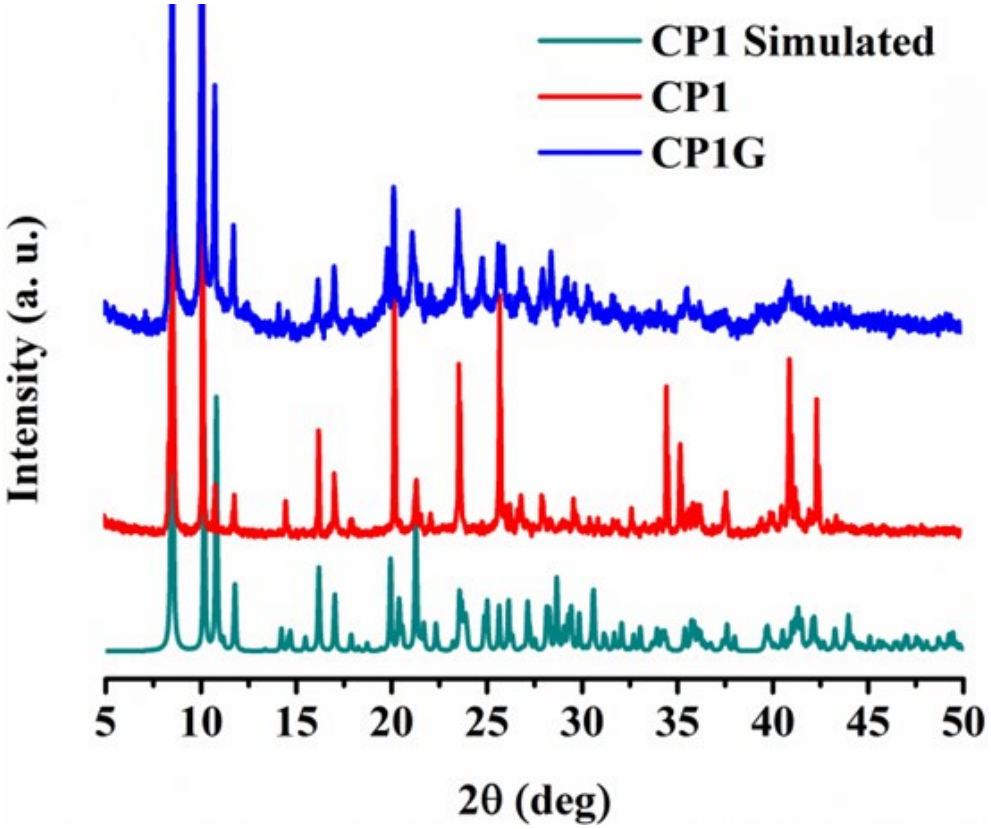
CPs	Bond	Angle (°)
CP1	Cu1-I1-Cu1	67.35(1)
	I1-Cu1-N11	110.78(5)
	I1-Cu1-I1	112.65(2)
	I1-Cu1-N21	106.53(6)
	N11-Cu1-I1	102.29(6)
	N11-Cu1-N21	119.90(8)
	I1-Cu1-N21	104.61(5)
	Cu1-N11-C11	128.88(17)
	Cu1-N11-C12	124.42(14)
	C21-N21-Cu1	123.00(18)
	C25-N21-Cu1	120.17(15)
CP2	Cu1-Br1-Cu1	74.05(2)
	Br1-Cu1-N2	111.22(5)
	Br1-Cu1-Br1	105.96(2)
	Br1-Cu1-N1	107.58(6)
	N2-Cu1-Br1	104.42(6)
	N2-Cu1-N1	122.72(7)
	Br1-Cu1-N1	103.44(6)
	C1-N1-Cu1	122.81(19)
	C5-N1-Cu1	120.46(16)
	Cu1-N2-C8	128.44(17)
	Cu1-N2-C9	125.39(13)
CP3	Cu2-I1-Cu1	73.56(8)
	Cu2-I1-Cu1	64.15(8)
	Cu1-I1-Cu1	101.37(9)
	Cu2-I2-Cu2	107.27(9)
	Cu2-I2-Cu1	74.63(8)
	Cu2-I2-Cu1	63.78(8)
	N11-Cu1-I1	117.2(5)
	N11-Cu1-I2	112.2(5)
	N11-Cu1-I1	110.0(5)
	I1-Cu1-I2	102.34(9)
	I1-Cu1-I1	101.37(9)
	I2-Cu1-I1	113.18(10)
	I1-Cu2-I2	109.12(10)
	I1-Cu2-N21	106.9(3)
	I1-Cu2-I2	118.30(10)
	I2-Cu2-N21	110.9(4)
	I2-Cu2-I2	107.27(10)
	N21-Cu2-I2	104.2(4)
	Cu1-N11-C11	128.7(15)
	Cu1-N11-C12	125.2(13)

Table S4. Hydrogen bonds in CPs

CPs	Donor-H···Acceptor	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
CP1	N12-H12···I1	0.88	2.86	3.4775(18)	129
	C17-H17···N21	0.95	2.59	3.475(3)	156
	C101-H10A···I1	0.98	3.25	3.839(3)	131
	C101-H10C··· I1	0.98	3.14	3.839(3)	130
	C24-H24···N100	0.95	2.70	3.495(4)	142
CP2	N3-H3···Br1	0.86	2.73	3.3336(18)	129
	C10-H10···N1	0.93	2.61	3.487(3)	157
	C1A-H1A3···Br1	0.96	2.92	3.741(3)	144
	C1A-H1A1···Br1	0.96	3.25	3.741(3)	132
	C4-H4···N1A	0.93	2.75	3.532(5)	143
CP3	N12-H12···O100	0.88	1.92	2.80(3)	179
	C26-H26···O100	0.95	2.33	3.27(3)	169
	C27-H27···I1	0.95	2.93	3.83(2)	157

Section S4: PXRD of CP1-3

(a)



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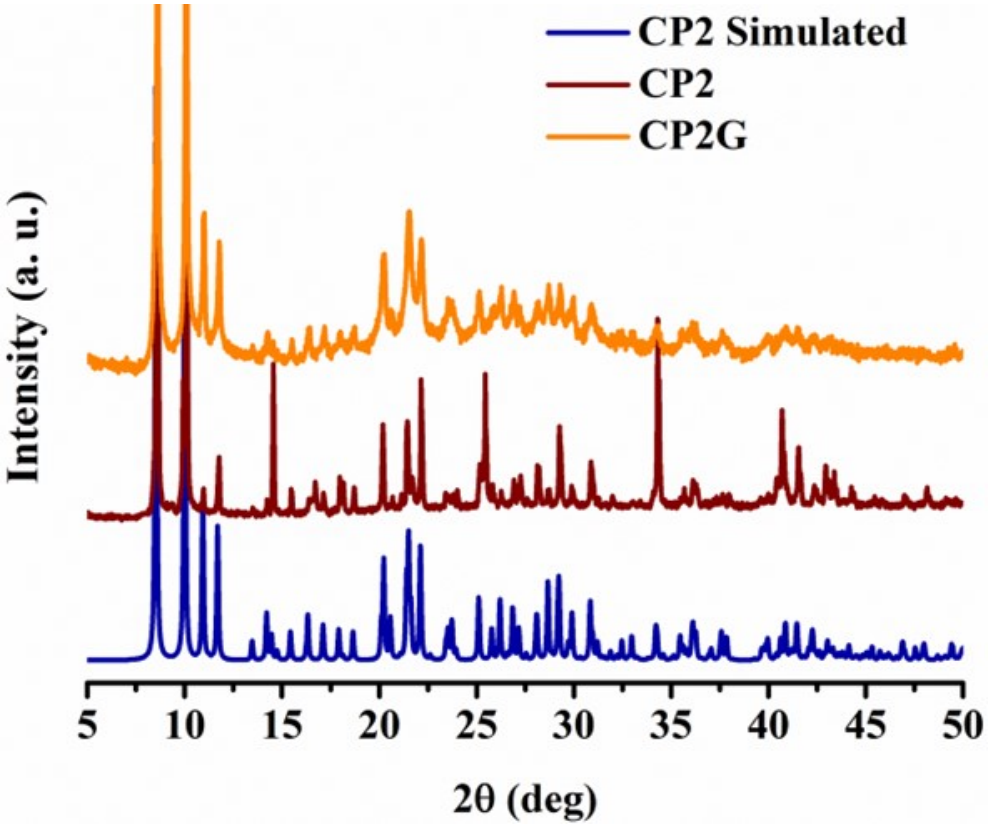

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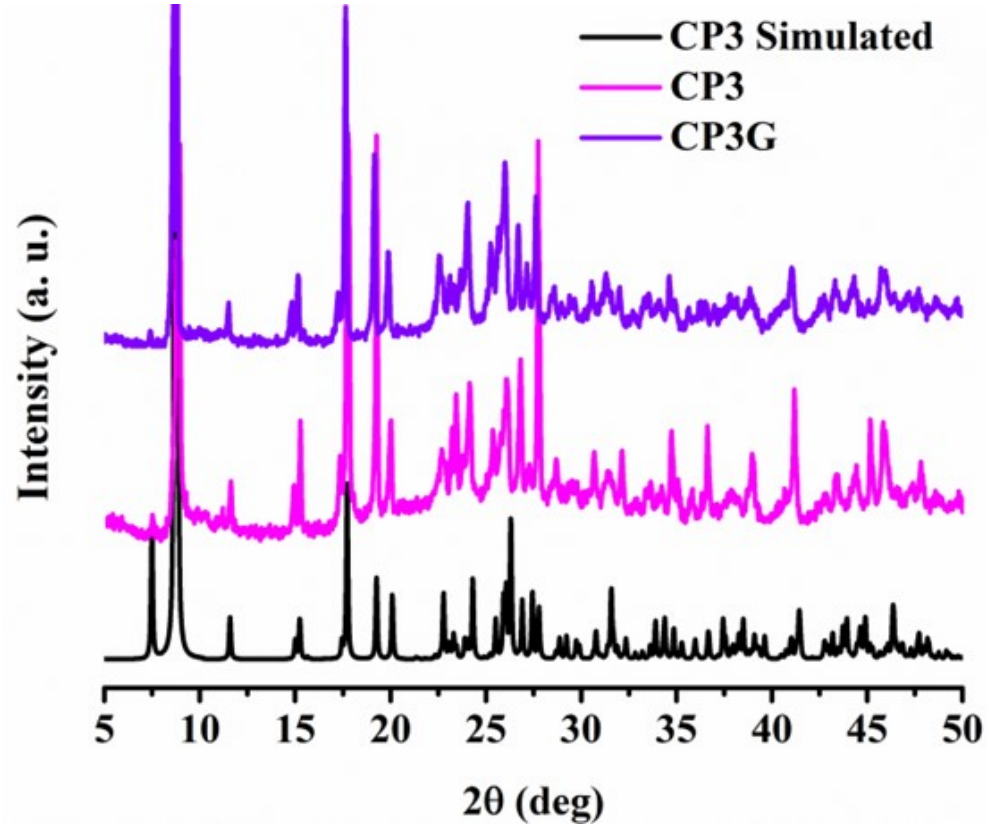

Figure S3. PXRD patterns of simulated, as-synthesized and ground CPs- (a) **CP1**, (b) **CP2**, (c) **CP3**.

Section S5: FT-IR of CPs

Table S5. Changes in FT-IR peaks for **CP1** and **CP2**

CP	Bonds	FT-IR frequency for As-synthesized CP (cm^{-1})	FT-IR frequency for ground CP (cm^{-1})	Changes found
CP1	C=N(pyridine)	1598	1602	Blue shifted
	C=C(pyridine)	1545	same	weakened
	C-N	1368	same	weakened
	C=C (bending)	1028	1031	Blue shifted and weakened
CP2	C=N(pyridine)	1598	1605	Blue shifted
	C=C(pyridine)	1545	same	weakened
	C-N	1372	same	weakened
	C=C (bending)	1029	1033	Blue shifted and weakened

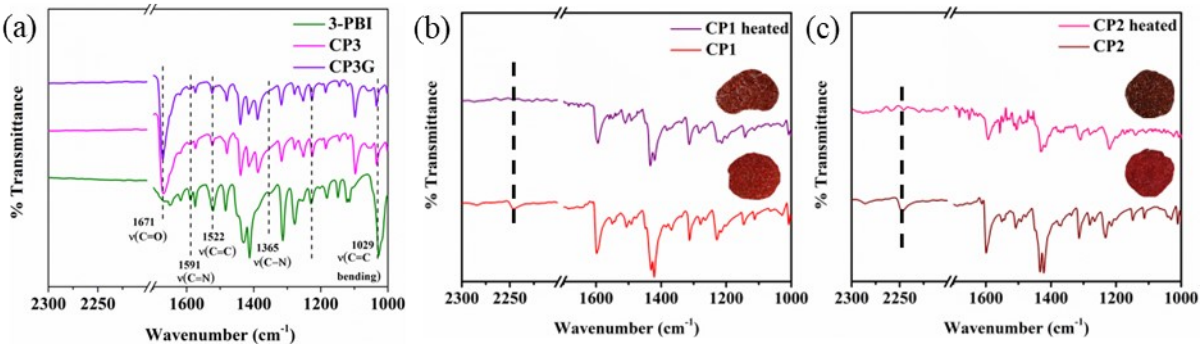

Figure S4. Comparison of FT-IR spectra of (a) 3-PBI, **CP3** and **CP3G**, (b) **CP1** before and after heating and (c) **CP2** before and after heating.

Section S6: TGA of the CPs

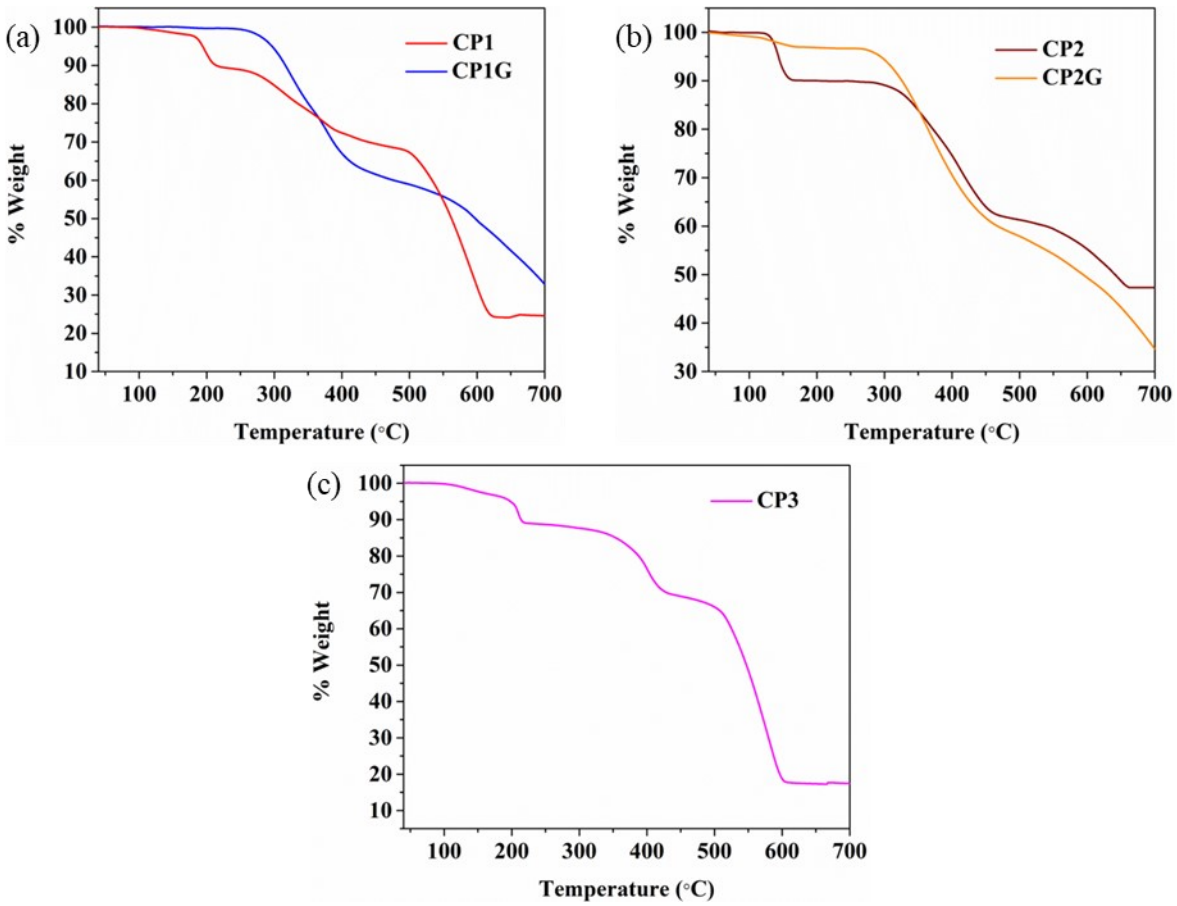

Figure S5. Thermogravimetric Analysis of (a) **CP1** and **CP1G**, (b) **CP2** and **CP2G** and (c) **CP3**.

Section S7: DRS of CP3

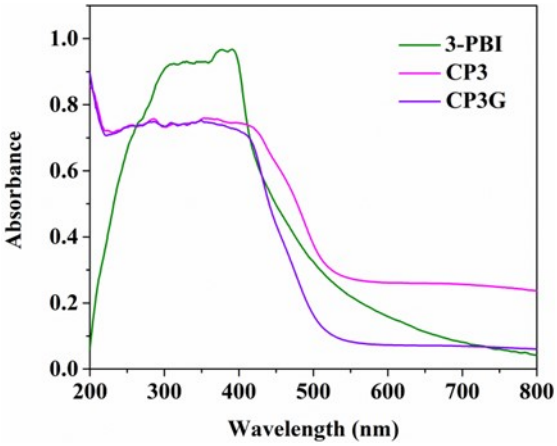

Figure S6. DRS of 3-PBI, **CP3** and **CP3G**.

Section S8: Solid state PL spectra of CP3

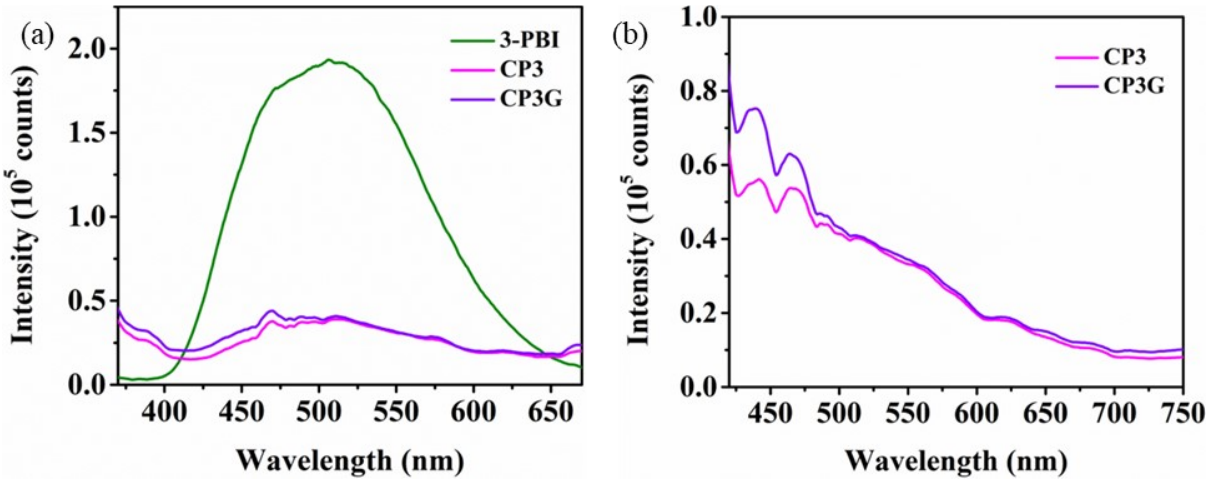

Figure S7. Solid state PL spectra of (a) 3-PBI, **CP3** and **CP3G** at 350 nm excitation, (b) **CP3** and **CP3G** at 400 nm excitation.

Section S9: Excitation spectra of CP1-3

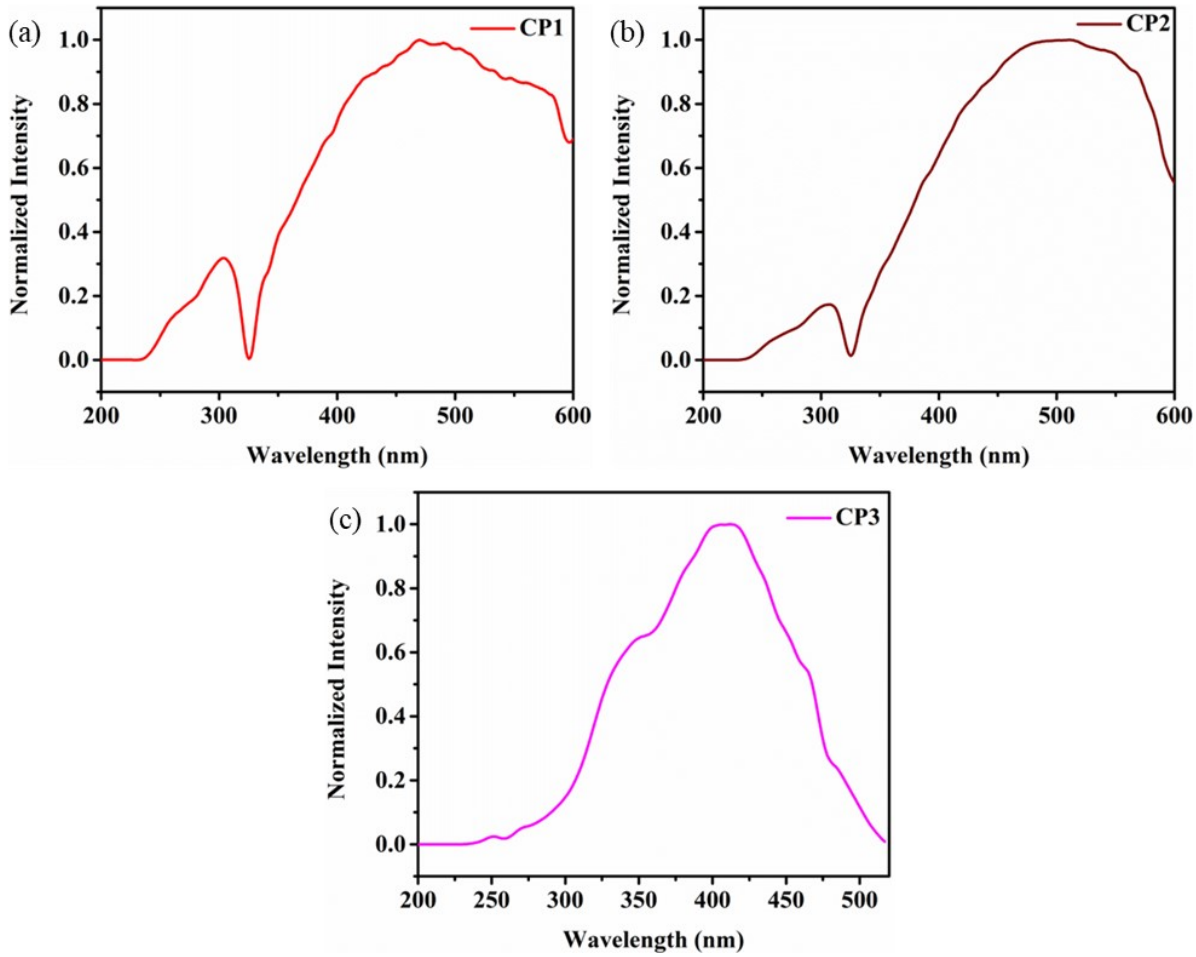

Figure S8. Excitation spectra of (a) **CP1**, (b) **CP2** and (c) **CP3**.

Section S10: CIE chromaticity diagrams of CP1-3

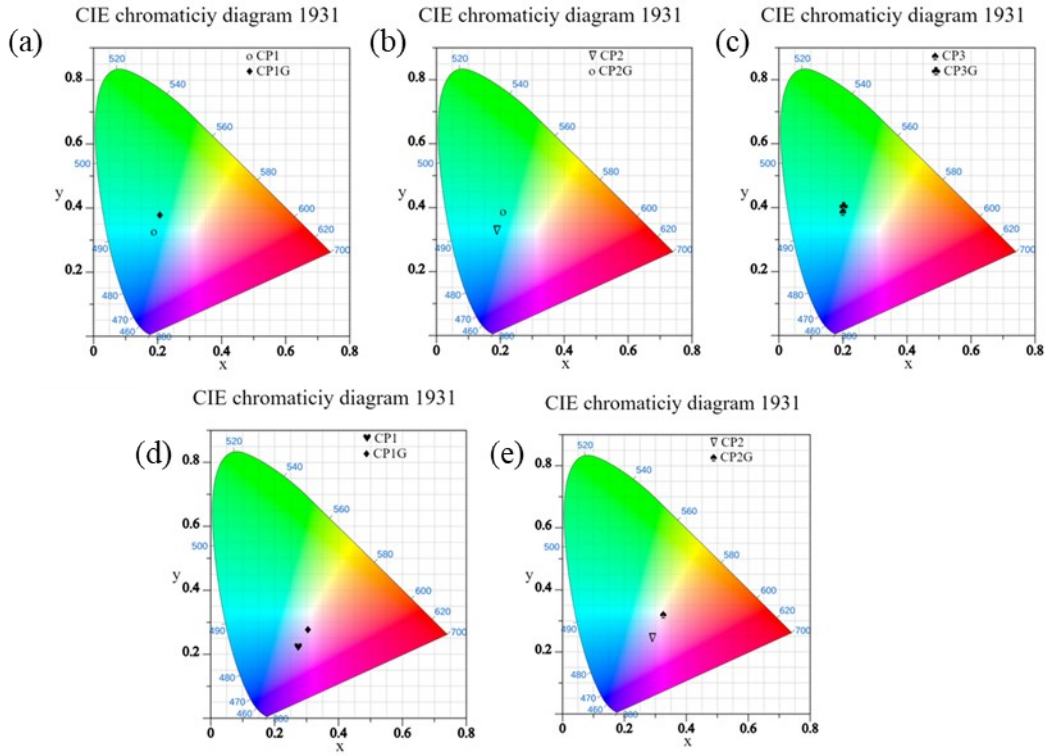

Figure S9. CIE chromaticity diagram of (a) **CP1**, (b) **CP2**, (c) **CP3**, (d) CP**1** and (e) **CP2** when excited to 420 nm.